

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

215149US0PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/926553

INTERNATIONAL APPLICATION NO.

PCT/JP00/03184

INTERNATIONAL FILING DATE

MAY 18, 2000

PRIORITY DATE CLAIMED

MAY 19, 1999 (Earliest)

TITLE OF INVENTION

PROCESS FOR PRODUCTION OF CATALYST

APPLICANT(S) FOR DO/EO/US

Toru KURODA, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☐ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

## Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Request for Priority

Request for Consideration of Documents Cited in International Search Report

PCT/IB/304

PCT/IB/308

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

09/926553

PCT/JP00/03184

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24. The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :**

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... **\$1040.00**
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... **\$890.00**
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... **\$740.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **\$710.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... **\$100.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =****\$890.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

**\$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	11 - 20 =	0	x \$18.00	<b>\$0.00</b>
Independent claims	1 - 3 =	0	x \$84.00	<b>\$0.00</b>
Multiple Dependent Claims (check if applicable)			<input type="checkbox"/>	<b>\$0.00</b>

**TOTAL OF ABOVE CALCULATIONS =****\$890.00**

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.

**\$0.00****SUBTOTAL =****\$890.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

**\$0.00****TOTAL NATIONAL FEE =****\$890.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

**\$0.00****TOTAL FEES ENCLOSED =****\$890.00**

Amount to be:

refunded

\$

charged

\$

- ☒ A check in the amount of **\$890.00** to cover the above fees is enclosed.
- ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030**. A duplicate copy of this sheet is enclosed.
- ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

(703) 413-3000  
(703) 413-2220

**Surinder Sachar**  
**Registration No. 34,423**

**22850**

SIGNATURE

**Norman F. Oblon**

NAME

**24,618**

REGISTRATION NUMBER

DATE

Nov. 19 2001

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215149US-0 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :

TORU KURODA ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW U.S. PCT APPLN :  
(BASED ON PCT/JP00/03184)

FILED: HERewith :

FOR: PROCESS FOR PRODUCTION OF  
CATALYSTPRELIMINARY AMENDMENTASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE SPECIFICATION

Please delete the paragraph beginning on page 32, line 24 through page 33, line 6, and replace with the following paragraph.

A reaction was conducted using this catalyst under the same conditions as in Reference Example 5. As a result, the conversion of methacrolein was 81.8%, the selectivity of methacrylic acid was 87.3% and the per-pass yield of methacrylic acid was 71.4%. Thus, the catalyst had performances equal to those of the catalyst of Reference Example 5 produced by an ordinary process.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

10. (Amended) A process for producing a catalyst according to Claim 1, wherein the recovery of molybdenum is 50 mass % or more and the recovery of the A element is 50 mass % or more.

REMARKS

Claims 1-11 are active in the present application. Claim 10 has been amended to remove multiple dependency. The specification has been amended to correct a typographical error. No new matter is believed to have been added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Norman F. Oblon  
Attorney of Record  
Registration No. 24,618

Daniel J. Pereira, Ph.D.  
Registration No. 45,518



**22850**

(703) 413-3000  
Fax #: (703) 413-2220  
NFO/DJPER/js  
I:\atty\SUKOS\215149US-PR.wpd

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**Marked-Up Copy**

Serial No: \_\_\_\_\_

Amendment Filed on: \_\_\_\_\_

11-19-01IN THE SPECIFICATION

Please delete the paragraph beginning on page 32, line 24 through page 33, line 6, and replace with the following paragraph.

--A reaction was conducted using this catalyst under the same conditions as in Reference Example 5. As a result, the conversion of methacrolein was 81.8%, the selectivity of methacrylic acid was 87.3% and the per-pass yield of methacrylic acid was 71.4%. Thus, the catalyst had performances equal to those of the catalyst of Reference Example [4] 5 produced by an ordinary process.

IN THE CLAIMS

10. (Amended) A process for producing a catalyst according to [any of Claims 1 to 9] Claim 1, wherein the recovery of molybdenum is 50 mass % or more and the recovery of the A element is 50 mass % or more.--

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## DESCRIPTION

## Process for Production of Catalyst

5

## Technical Field

The present invention relates to a process for producing a catalyst using a compound recovered from a used catalyst, as a material for elements constituting the catalyst to be produced.

10

## Background Art

A catalyst containing at least molybdenum, an A element (at least one element selected from the group consisting of phosphorus and arsenic) and an X element (at least one element selected from the group consisting of potassium, rubidium and cesium) can be used for production of methacrylic acid by gas phase catalytic oxidation of methacrolein, production of methacrylic acid by oxidative dehydration of isobutyric acid, and other purpose.

20

In JP-A-53-113790 and JP-A-63-130144 are described processes for producing a catalyst using, as a material, a compound obtained by treating, with ammonia solution or the like, a used catalyst having a composition such as mentioned above, which used

25

catalyst has been used for production of methacrylic acid by gas phase catalytic oxidation of methacrolein.

However, the catalysts produced by the processes described in JP-A-53-113790 and JP-A-63-130144 are different in structure from virgin catalysts produced by an ordinary process and therefore have shown low catalytic performances in some cases.

#### 10 Disclosure of the Invention

Hence, in order to effectively utilize a used catalyst containing at least molybdenum, an A element (at least one element selected from the group consisting of phosphorus and arsenic) and an X  
15 element (at least one element selected from the group consisting of potassium, rubidium and cesium), the present invention aims at providing a process for producing a catalyst using, as a material, a compound containing at least molybdenum and said A element,  
20 which has been recovered from a used catalyst having a composition such as mentioned above.

The gist of the present invention lies in a process for producing a catalyst, which comprises dispersing, in water, a used catalyst containing at  
25 least molybdenum, an A element (at least one element

selected from the group consisting of phosphorus and arsenic) and an X element (at least one element selected from the group consisting of potassium, rubidium and cesium), adding thereto an alkali metal compound and/or ammonia solution, then adjusting the resulting mixture to pH 6.5 or less to generate a precipitate containing at least said molybdenum and said A element, and using the precipitate as a material for catalyst-constituting elements.

According to the present invention, it is possible to produce a catalyst using, as a material, a compound which has been recovered from a used catalyst containing at least molybdenum, an A element and an X element and which contains at least molybdenum and the A element; thereby, the used catalyst can be utilized effectively.

The present invention is particularly useful in producing a catalyst of a formula (1) (shown later) for production of methacrylic acid by gas phase catalytic oxidation of methacrolein, using a material recovered from a used catalyst which was, before the use, a catalyst of the formula (1) for production of methacrylic acid by gas phase catalytic oxidation of methacrolein.

According to the present invention, in

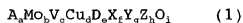


recovering the compound containing at least molybdenum and the A element, molybdenum and the A element can be recovered at high ratios; therefore, the used catalyst can be utilized effectively.

5

#### Best Mode for Carrying Out the Invention

In the present invention, the used catalyst containing at least molybdenum, an A element and an X element includes catalysts which have been used in,  
10 for example, production of methacrylic acid by gas phase catalytic oxidation of methacrolein or production of methacrylic acid by oxidative dehydrogenation of isobutyric acid. A catalyst for use in production of methacrylic acid preferably has  
15 a composition represented by the following formula (1):



(wherein Mo, V, Cu and O are molybdenum, vanadium, copper and oxygen, respectively; A is at least one  
20 element selected from the group consisting of phosphorus and arsenic; D is at least one element selected from the group consisting of antimony, bismuth, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; X is at least  
25 one element selected from the group consisting of

potassium, rubidium and cesium; Y is at least one element selected from the group consisting of iron, zinc, chromium, magnesium, tantalum, manganese, cobalt, barium, gallium, cerium and lanthanum; Z is sodium and/or thallium; a, b, c, d, e, f, g, h and i are each the atomic ratio of each element; when b is 12,  $a=0.5$  to 3,  $c=0.01$  to 3,  $d=0$  to 2,  $e=0$  to 3,  $f=0.01$  to 3,  $g=0$  to 3,  $h=0$  to 3, and i is the atomic ratio of oxygen necessary for satisfying the valency of each component other than oxygen).

The used catalyst containing at least molybdenum, an A element and an X element is first dispersed in water. Thereto is added an alkali metal compound and/or ammonia solution. The amount of the alkali metal compound and/or ammonia solution added may be such that the molybdenum, A element and X element are dissolved; however, the amount is preferably such that the resulting mixture has a pH of 8 or more, more preferably such that the mixture has a pH of 8.5 to 12. The alkali metal compound usable has no particular restriction as to the kind; however, there can be mentioned, for example, sodium hydroxide, potassium hydroxide, cesium hydroxide and sodium hydrogencarbonate, with sodium hydroxide being preferred particularly.

Next, to the mixture after addition of the alkali metal compound and/or ammonia solution is added an acid for pH adjustment to 6.5 or less. It is preferable that, prior to the pH adjustment, the insolubles in the mixture are removed by filtration or the like. As the acid added for pH adjustment, there can be mentioned, for example, hydrochloric acid, nitric acid and sulfuric acid, with hydrochloric acid and nitric acid being preferred particularly.

The material after pH adjustment is preferably kept for a given time for formation of a precipitate. The time of keeping is preferably about 0.5 to 24 hours, and the liquid temperature is preferably about 15 normal temperature to 90°C. During the keeping, the material may be allowed to stand but preferably is stirred.

The precipitate formed by pH adjustment, i.e. the compound containing at least molybdenum and an A element is presumed, from the compositional analysis and X-ray diffractometry, to contain, as the main component, a Dawson type heteropolyacid salt having a central element (e.g. phosphorus) and molybdenum ratio of 2:18, or a mixture of a Keggin type heteropolyacid salt having a central element (e.g.

phosphorus) and molybdenum ratio of 1:12 and a Dawson type heteropolyacid. As the adjusted pH is lower, the proportion of the Keggin type heteropolyacid salt is larger.

- 5           When the proportion of each element contained in the precipitate formed from the used catalyst, relative to the amount of each element contained in the used catalyst is defined as the recovery of each element, the recovery of each element varies
- 10 depending upon the composition of the used catalyst, the amount of ammonium root in the mixture before pH adjustment, and the adjusted pH. In the case of, for example, a used catalyst having a composition of the above-mentioned formula (1), the A element recovered
- 15 in the form of a heteropolyacid salt of Keggin type is mostly phosphorus. Meanwhile, the A element recovered in the form of a heteropolyacid salt of Dawson type is phosphorus and arsenic; however, when both of them are present, arsenic is recovered
- 20 preferentially. Therefore, in a used catalyst having a composition containing both phosphorus and arsenic, the adjustment of pH is preferably made to 1.5 or less in order to recover phosphorus preferentially, and to 2 to 6.5 in order to recover arsenic
- 25 preferentially. In determining the pH to be adjusted,

it is desirable to consider the recoveries of individual elements including molybdenum, etc.

In the present invention, the recovery of molybdenum can thus be made preferably 50 mass % or  
5 more, more preferably 70 mass % or more. Also, the recovery of the A element can be made preferably 50 mass % or more, more preferably 70 mass % or more.

When the amount of the X element is not sufficient to precipitate a heteropolyacid in the  
10 form of a salt of the X element, it is preferred that a raw material for ammonium root is added before the adjustment of pH so that the ammonium root is present in an amount of 0.5 mole or more, preferably 3 to 40 moles per mole of the A element. By this addition, a  
15 higher amount of a heteropolyacid can be precipitated in the form of an ammonium salt, and the molybdenum and the A element contained in the precipitate can be recovered at higher recoveries. A higher amount of the ammonium root results in higher recoveries of  
20 molybdenum and the A element. The kind of the ammonium root is not particularly restricted as long as it is soluble; and there can be mentioned, for example, ammonia solution, ammonium chloride, ammonium nitrate and ammonium carbonate.

25 The thus-precipitated compound contains

molybdenum, the A element and, further, the X element.

The presence of the X element in the compound is desirably a small amount or zero in some cases, depending upon the application of the compound. In

- 5 such cases, the whole or part of the X element is preferably removed from the mixture before the pH adjustment to 6.5 or less.

There is no particular restriction as to the method for removing the X element. However, there

- 10 can be mentioned, for example, a method of removing the X ion by its adsorption on an cation exchange resin. As the cation exchange resin, there can be used, for example, a styrene type resin and a chelate resin which are each an ordinary strongly acidic  
15 cation exchange resin, and a Na type ion exchange resin is preferred particularly. As to the timing of removal of the X element, there is no particular restriction as long as it is before the pH adjustment to 6.5 or less; however, removal of the X element is  
20 preferably made according to the following procedure.

That is, a used catalyst containing at least molybdenum, the A element and the X element is dispersed in water; thereto is added sodium hydroxide for dissolution; as necessary, the resulting

- 25 insolubles are removed by filtration or the like; the

X element is removed using a cation exchange resin or the like; a material for ammonium root is added in an amount of 0.5 mole or more per mole of the A element; then, an acid is added for pH adjustment to 6.5 or less.

There is no particular restriction as to the method for separating the precipitate formed by the pH adjustment, from the liquid containing the precipitate, and there can be mentioned ordinary methods such as filtration (e.g. gravity filtration, pressure filtration, vacuum filtration or filter press), centrifugation and the like. The precipitate may be washed as necessary in order to remove impurities from the precipitate. The solution for this washing is selected in view of the application and solubility of the precipitate, and there can be mentioned, for example, pure water and a dilute aqueous solution of ammonium nitrate, ammonium chloride or the like.

In the present invention, the thus-obtained precipitate is used as a material for catalyst. In this case, the state of the precipitate is not particularly restricted and may be a wet state or a dry state. Also, an oxide obtained by calcining the precipitate may be used when it is desired to use the

material for catalyst in the form of an oxide. The calcination temperature is preferably 200 to 700°C.

In the present invention, the process for producing a catalyst is not particularly restricted  
5 and can be appropriately selected from various well known processes such as evaporation to dryness, precipitation, oxides mixing and the like, depending upon the state of the precipitate used as a material.

The catalyst produced in the present invention  
10 contains at least molybdenum, an A element and an X element. Meanwhile, an ordinary catalyst further contains other elements so that the composition thereof is suitable for an intended reaction. For example, a catalyst used for production of  
15 methacrylic acid by gas phase catalytic oxidation of methacrolein, preferably has a composition of the previously-mentioned formula (1); in producing such a catalyst, materials other than the above-mentioned precipitate are also used. As such materials, there  
20 are mentioned oxides, nitrates, carbonates, ammonium salts, halides, etc. of the individual elements constituting the catalyst to be produced. As materials of, for example, molybdenum, there are mentioned ammonium paramolybdate, molybdenum trioxide,  
25 etc.



In producing a catalyst, there is first prepared a solution or aqueous slurry containing all materials for catalyst (the solution or slurry is hereinafter referred to as mixed solution). The mixed solution is subjected as necessary to drying, filtration, water content control by heating, or the like. The drying can be conducted by ordinary evaporation to dryness by heating, vacuum drying, air drying, or the like, and the temperature for drying is preferably 60 to 150°C.

Next, the thus-obtained mixed solution, water content-controlled mixed solution or dried material is shaped. The shaping in the present invention includes mechanical shaping using an ordinary powder molding machine such as tableting machine, extrusion molding machine, tumbling granulator or the like; loading shaping of loading a catalyst component(s) on a carrier; drying shaping using a spray dryer, a drum dryer, a slurry dryer or the like; and so forth. There is no particular restriction as to the method for shaping.

The shape after shaping can be determined as desired, and it can be spherical, ring-shaped, columnar, hollow-spherical, flake-like, stellar, etc. As the carrier used in loading shaping, there can be

mentioned, for example, inactive carriers such as silica, alumina, silica-alumina, magnesia, titania, silicon carbide and the like. An additive may be added in the shaping. Such an additive includes, for example, organic compounds such as polyvinyl alcohol, carboxymethyl cellulose and the like; inorganic compounds such as graphite, diatomaceous earth and the like; and inorganic fibers such as glass fiber, ceramic fiber, carbon fiber and the like.

10 The shaped catalyst is then subjected to a heat treatment. The conditions of the heat treatment are not particularly restricted and can be known treatment conditions. For example, in the case of a catalyst for production of methacrylic acid by gas  
15 phase catalytic oxidation of methacrolein, the temperature of the heat treatment is preferably 300 to 500°C and it is preferred to conduct the heat treatment in an air stream or in a moisture-controlled air stream.

20 The catalyst produced according to the process of the present invention may be used by dilution with an inert carrier such as silica, alumina, silica-alumina, magnesia, titania, silicon carbide, stainless steel or the like.

25 When the catalyst produced according to the

present process is used in a reaction, the reaction conditions are not particularly restricted and known reaction conditions can be used. Below are mentioned the reaction conditions when methacrylic acid is  
5 produced by gas phase catalytic oxidation of methacrolein.

The concentration of methacrolein in the raw material gas can be varied in a wide range but is preferably 1 to 20% by volume, particularly  
10 preferably 3 to 10% by volume. As the oxygen source in the raw material gas, air is economical and oxygen-enriched air may be used as necessary. The oxygen concentration in the raw material gas is preferably 0.3 to 4 moles, particularly preferably  
15 0.4 to 2.5 moles per mole of methacrolein. The material gas may be diluted with an inert gas such as nitrogen, steam, carbon dioxide or the like. The reaction pressure may vary from normal pressure to several atm. The raw material gas may contain a  
20 small amount of impurities such as lower saturated aldehydes and the like, and these impurities gives substantially no adverse effect on the reaction. The reaction temperature can be selected in a range of 230 to 450°C, particularly preferably in a range of  
25 250 to 400°C. The reaction may be conducted in a

fixed bed or in a fluidized bed.

By conducting a reaction using a catalyst obtained by the production process of the present invention, it is possible to achieve a conversion which is preferably 90% or more, more preferably 95% or more of the conversion obtained using a virgin catalyst. It is also possible to achieve a selectivity which is preferably 90% or more, more preferably 95% or more of the selectivity obtained using a virgin catalyst. It is further possible to achieve a per-pass yield which is preferably 90% or more, more preferably 95% or more of the per-pass yield obtained using a virgin catalyst.

Hereinafter, the present invention is described using Examples. In the Examples, "part(s)" is/are part(s) by mass; and the quantitative analyses of contained elements (or molecules) were made by ICP emission spectrometry, atomic absorption spectrometry, ion chromatography and Kjeldahl method. The quantitative analyses of raw material gas and product in production of methacrylic acid were made using gas chromatography. The recovery of each element, the conversion of methacrolein, and the selectivity and per-pass yield of methacrylic acid produced were calculated using the following formulas.

Recovery (%) =

$$\frac{[(\text{mass of element contained in obtained compound})/(\text{mass of element contained in used catalyst})] \times 100}{}$$

5 Conversion of methacrolein (%) =

$$\frac{[(\text{moles of reacted methacrolein})/(\text{moles of fed methacrolein})] \times 100}{}$$

Selectivity of methacrylic acid (%) =

10 
$$\frac{[(\text{moles of produced methacrylic acid})/(\text{moles of reacted methacrolein})] \times 100}{}$$

Per-pass yield of methacrylic acid (%) =

$$\frac{[(\text{moles of produced methacrylic acid})/(\text{moles of fed methacrolein})] \times 100}{}$$

15 [Reference Example 1]

In 300 parts of pure water were dissolved, at 70°C, 63.62 parts of ammonium paramolybdate, 1.05 parts of ammonium metavanadate and 7.61 parts of cesium nitrate. Thereto was added a solution of 3.46  
20 parts of 85 mass % phosphoric acid dissolved in 10 parts of pure water, followed by addition of 1.31 parts of antimony trioxide. The resulting mixture was heated to 95°C with stirring. Then, a solution of 1.45 parts of copper nitrate dissolved in 10 parts  
25 of pure water was added, and the resulting mixture

was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed, and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air stream to obtain a catalyst. This catalyst had a composition of  $P_{1.1}Mo_{12}V_{0.3}Sb_{0.3}Cu_{0.2}Cs_{1.3}$ .

The catalyst was charged into a reaction tube.

- 10 Through the reaction tube was passed a mixed gas consisting of 5% by volume of methacrolein, 10% by volume of oxygen, 30% by volume of steam and 55% by volume of nitrogen, at a reaction temperature of 270°C for a contact time of 3.6 seconds to conduct a
- 15 reaction. As a result, the conversion of methacrolein was 80.8%, the selectivity of methacrylic acid was 81.2% and the per-pass yield of methacrylic acid was 65.6%.

[Example 1]

- 20 In 400 parts of pure water was dispersed 87 parts of a used catalyst which had been used in a reaction for 2,000 hours under the same reaction conditions as in Reference Example 1 and which contained 34.54 parts of molybdenum, 0.93 part of
- 25 phosphorus and 5.18 parts of cesium and had an

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oxygen-excluded composition (hereinafter,  
"composition" refers to an oxygen-excluded  
composition) of  $P_1Mo_{12}Cs_{1.1}$ . Thereto was added 68.2  
parts of 25 mass % ammonia solution (ammonia root  
5 amount = 2.77 moles per mole of molybdenum) and the  
resulting mixture was stirred for 1 hour. Thereto  
was added 107.1 parts of 36 mass % hydrochloric acid  
for pH adjustment to 2.0. The resulting solution was  
kept at 35°C for 3 hours with stirring. The  
10 resulting precipitate was collected by filtration and  
washed with a 2 mass % ammonium nitrate solution to  
obtain a "recovered compound 1". The recovered  
compound 1 contained 34.19 parts of molybdenum, 0.93  
part of phosphorus, 5.14 parts of cesium, and 0.19  
15 mole, per mole of molybdenum, of ammonium root. The  
recoveries of individual elements were 99.0%  
(molybdenum), 100% (phosphorus) and 99.2% (cesium).

The recovered compound 1 was added to 250 parts  
of pure water. The resulting mixture was heated to  
20 60°C with stirring. Thereto were added, in the  
following order, a solution of 0.70 part of ammonium  
paramolybdate, 0.07 part of cesium nitrate and 13.57  
parts of 25 mass % ammonia solution dissolved in 50  
parts of pure water, 1.05 parts of ammonium  
25 metavanadate and 1.31 parts of antimony trioxide.

The resulting mixture was heated to 95°C with stirring. Next, there were added a solution of 1.45 parts of copper nitrate dissolved in 10 parts of pure water and a solution of 3.10 parts of ammonium nitrate dissolved in 10 parts of pure water. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air stream, to obtain a catalyst. The catalyst had the same composition as in Reference Example 1, i.e.

$$\text{P}_1\text{Mo}_{12}\text{V}_{0.3}\text{Sb}_{0.3}\text{Cu}_{0.2}\text{Cs}_{1.3}.$$

A reaction was conducted using this catalyst under the same conditions as in Reference Example 1. As a result, the conversion of methacrolein was 80.7%, the selectivity of methacrylic acid was 81.5% and the per-pass yield of methacrylic acid was 65.8%. Thus, the catalyst had performances equal to those of the catalyst of Reference Example 1 produced by an ordinary process.

[Reference Example 2]

In 300 parts of pure water were dissolved, at 50°C, 63.62 parts of ammonium paramolybdate, 1.76



parts of ammonium metavanadate and 3.64 parts of potassium nitrate. Thereto was added a solution of 3.46 parts of 85 mass % phosphoric acid dissolved in 10 parts of pure water, followed by addition of a  
5 solution of 2.06 parts of gallium nitrate (Ga content = 20.3% by mass) dissolved in 10 parts of pure water. The resulting mixture was heated to 95°C. Thereto were added, in the following order, a solution of 2.18 parts of copper nitrate dissolved in 10 parts of  
10 pure water, a solution of 0.93 part of boric acid dissolved in 10 parts of pure water and a solution of 1.72 parts of manganese nitrate dissolved in 10 parts of pure water. The resulting mixture was evaporated to dryness with heating and stirring. The solid  
15 obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed, and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air stream to obtain a catalyst. This catalyst  
20 had a composition of  $P_1MO_{1.2}V_{0.5}Cu_{0.3}Ga_{0.2}B_{0.5}Mn_{0.2}K_{1.2}$ .

A reaction was conducted using this catalyst under the same conditions as in Reference Example 1. As a result, the conversion of methacrolein was 90.5%, the selectivity of methacrylic acid was 89.7% and the  
25 per-pass yield of methacrylic acid was 81.2%.

[Example 2]

In 400 parts of pure water was dispersed 91 parts of a used catalyst which had been used in a reaction for 2,000 hours under the same reaction conditions as in Reference Example 1 and which contained 34.54 parts of molybdenum, 0.93 part of phosphorus, 1.41 parts of potassium, 0.76 part of vanadium and 0.57 part of copper and had a composition of  $P_1Mo_{1.1}K_{1.2}V_{0.5}Cu_{0.3}$ . Thereto was added 89.0 parts of a 45 mass % sodium hydroxide solution, and the resulting mixture was stirred for 1 hour. Then, the insolubles were removed by filtration. To the filtrate was added 127.2 parts of 36 mass % hydrochloric acid for pH adjustment to 1.0. The resulting solution was kept at 30°C for 3 hours with stirring. The resulting precipitate was collected by filtration and washed with pure water to obtain a "recovered compound 2". The recovered compound 2 contained 20.72 parts of molybdenum, 0.52 part of phosphorus, 1.22 parts of potassium and 0.07 part of vanadium. The recoveries of individual elements were 60.0% (molybdenum), 55.9% (phosphorus), 86.5% (potassium) and 9.2% (vanadium).

In 300 parts of pure water were dissolved, at 50°C, 25.49 parts of ammonium paramolybdate, 1.60

parts of ammonium metavanadate and 0.49 part of potassium nitrate. To the solution being stirred was added the recovered compound 2. Then, a solution of 1.53 parts of 85 mass % phosphoric acid dissolved in 10 parts of pure water was added. Thereto was added 12.70 parts of 25 mass % ammonia solution, followed by addition of a solution of 2.06 parts of gallium nitrate (Ga content = 20.3% by mass) dissolved in 10 parts of pure water. The resulting mixture was heated to 95°C. Subsequently, there were added, in the following order, a solution of 3.35 parts of copper nitrate dissolved in 30 parts of pure water, a solution of 0.93 part of boric acid dissolved in 10 parts of pure water, a solution of 1.72 parts of manganese nitrate dissolved in 10 parts of pure water and 31.2 parts of 6.1 mass % nitric acid. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air stream, to obtain a catalyst. The catalyst had the same composition as in Reference Example 2, i.e.

$P_1Mo_{12}V_{0.5}Cu_{0.5}Ga_{0.2}B_{0.5}Mn_{0.2}K_{1.2}$ .

A reaction was conducted using this catalyst under the same conditions as in Reference Example 1. As a result, the conversion of methacrolein was 90.1%, the selectivity of methacrylic acid was 89.8% and the per-pass yield of methacrylic acid was 80.9%. Thus, the catalyst had performances equal to those of the catalyst of Reference Example 2 produced by an ordinary process.

[Reference Example 3]

10 To 400 parts of pure water were added 50.75 parts of molybdenum trioxide, 1.34 parts of vanadium pentoxide and 3.39 parts of 85 mass % phosphoric acid. The resulting mixture was stirred for 3 hours under refluxing. Thereto was added 0.70 part of copper  
15 oxide, followed by stirring for 2 hours under refluxing. The mixed solution after refluxing was cooled to 50°C. Thereto were added a solution of 3.56 parts of potassium nitrate dissolved in 20 parts of pure water and then a solution of 5 parts of  
20 ammonium nitrate dissolved in 20 parts of pure water. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed, and sifted  
25 using a sieve to separate a moiety of 0.85 to 1.70 mm.

It was heat-treated at 370°C for 3 hours in an air stream to obtain a catalyst. This catalyst had a composition of  $P_1Mo_{12}V_{0.5}Cu_{0.3}K_{1.2}$ .

A reaction was conducted using this catalyst  
5 under the same conditions as in Reference Example 1 except that the reaction temperature was 285°C. As a result, the conversion of methacrolein was 85.0%, the selectivity of methacrylic acid was 84.2% and the per-pass yield of methacrylic acid was 71.6%.

10 [Example 3]

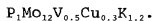
91 parts of the same used catalyst as in Example 2 was dispersed in 400 parts of pure water. Thereto was added 89.0 parts of a 45 mass % sodium hydroxide solution. The resulting mixture was  
15 stirred for 1 hour. The insolubles were removed by filtration. The filtrate was passed through a styrene type strongly acidic cation exchange resin made into a Na type, i.e. Amberlite IR-120B (a product of Organo Corporation), at SV = 1 to remove  
20 potassium. To the solution after passing was added 29.1 parts of 36 mass % hydrochloric acid for pH adjustment to 8.9. Then, 19.25 parts of ammonium chloride (ammonium root amount = 1.00 mole per mole of molybdenum) was added. Thereafter, 84.6 parts of  
25 36 mass % hydrochloric acid was added for pH

000255Z JUL 60  
10 adjustment to 1.0. The resulting mixture was kept at 25°C for 3 hours with stirring. The resulting precipitate was collected by filtration, washed with a 2 mass % ammonium nitrate solution, dried at 130°C for 16 hours, and calcined at 400°C for 5 hours in an air stream to obtain a "recovered compound 3". The recovered compound 3 contained 32.74 parts of molybdenum, 0.91 part of phosphorus and 0.67 part of vanadium. The recoveries of individual elements were 94.8% (molybdenum), 97.8% (phosphorus) and 88.2% (vanadium).

To 400 parts of pure water were added 1.63 parts of molybdenum trioxide, 0.14 part of vanadium pentoxide and the recovered compound 3. The resulting mixture was stirred for 3 hours under refluxing. Thereto was added 0.70 part of copper oxide, followed by stirring for 2 hours under refluxing. The mixed solution after refluxing was cooled to 50°C. Thereto were added a solution of 3.56 parts of potassium nitrate dissolved in 20 parts of pure water and further a solution of 5 parts of ammonium nitrate dissolved in 20 parts of pure water. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was

subjected to pressure molding, crushed and sifted  
using a sieve to separate a moiety of 0.85 to 1.70 mm.

It was heat-treated at 370°C for 3 hours in an air  
stream, to obtain a catalyst. The catalyst had the  
5 same composition as in Reference Example 3, i.e.



A reaction was conducted using this catalyst  
under the same conditions as in Reference Example 3.

As a result, the conversion of methacrolein was 84.9%,  
10 the selectivity of methacrylic acid was 84.8% and the  
per-pass yield of methacrylic acid was 72.0%. Thus,  
the catalyst had performances equal to those of the  
catalyst of Reference Example 3 produced by an  
ordinary process.

15 [Reference Example 4]

In 300 parts of pure water were dissolved, at  
60°C, 63.52 parts of ammonium paramolybdate, 1.05  
parts of ammonium metavanadate and 7.60 parts of  
cesium nitrate. To the solution being stirred was  
20 added a solution of 3.46 parts of 85 mass %  
phosphoric acid and 3.55 parts of 60 mass % arsenic  
acid dissolved in 20 parts of pure water. Further,  
0.63 part of germanium dioxide was added. The  
resulting mixture was heated to 95°C. Then, a  
25 solution of 1.78 parts of zinc nitrate dissolved in

10 parts of pure water was added. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to  
5 pressure molding, crushed, and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air stream to obtain a catalyst. This catalyst had a composition of  $P_1Mo_{12}V_{0.3}As_{0.5}Ge_{0.2}Zn_{0.2}Cs_{1.3}$ .

10 A reaction was conducted using this catalyst under the same conditions as in Reference Example 1 except that the reaction temperature was 290°C. As a result, the conversion of methacrolein was 85.3%, the selectivity of methacrylic acid was 85.2% and the  
15 per-pass yield of methacrylic acid was 72.7%.

[Example 4]

In 400 parts of pure water was dispersed 89 parts of a used catalyst which had been used in a reaction for 2,000 hours under the same reaction  
20 conditions as in Reference Example 1 and which contained 34.54 parts of molybdenum, 0.93 part of phosphorus, 5.18 parts of cesium and 1.12 parts of arsenic and had a composition of  $P_1Mo_{12}As_{0.5}Cs_{1.3}$ . Thereto was added 89.0 parts of a 45 mass % sodium  
25 hydroxide solution, followed by stirring for 1 hour.



Thereto was added 32.5 parts of 36 mass %  
hydrochloric acid for pH adjustment to 7.5. Thereto  
was added 28.90 parts of ammonium chloride (ammonium  
root amount = 1.50 moles per mole of molybdenum),  
5 followed by addition of 55.6 parts of 36 mass %  
hydrochloric acid for pH adjustment to 4.0. The  
resulting mixture was kept at 30°C for 3 hours with  
stirring. The resulting precipitate was collected by  
filtration and washed with a 2 mass % ammonium  
10 nitrate solution to obtain a "recovered compound 4".  
The recovered compound 4 contained 23.94 parts of  
molybdenum, 0.48 part of phosphorus, 5.14 parts of  
cesium, 1.12 parts of arsenic and 0.48 mole, per mole  
of molybdenum, of ammonium root. The recoveries of  
15 individual elements were 69.3% (molybdenum), 51.6%  
(phosphorus), 99.2% (cesium) and 100% (arsenic).

In 300 parts of pure water were dissolved, at  
60°C, 19.46 parts of ammonium paramolybdate, 1.05  
parts of ammonium metavanadate and 0.06 part of  
20 cesium nitrate. To the solution being stirred was  
added the recovered compound 4. Then, a solution of  
1.67 parts of 85 mass % phosphoric acid dissolved in  
10 parts of pure water was added. Thereto was added  
6.41 parts of 25 mass % ammonia solution, followed by  
25 addition of 0.63 part of germanium dioxide. The

resulting mixture was heated to 95°C. Then, there were added a solution of 1.78 parts of zinc nitrate dissolved in 10 parts of pure water and 39.9 parts of 6.1 mass % nitric acid. The resulting mixture was

5 evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for

10 5 hours in an air stream, to obtain a catalyst. The catalyst had the same composition as in Reference Example 4, i.e.  $P_1Mo_{12}V_{0.3}As_{0.5}Ge_{0.2}Zn_{0.2}Cs_{1.3}$ .

A reaction was conducted using this catalyst under the same conditions as in Reference Example 4.

15 As a result, the conversion of methacrolein was 85.3%, the selectivity of methacrylic acid was 85.5% and the per-pass yield of methacrylic acid was 72.9%. Thus, the catalyst had performances equal to those of the catalyst of Reference Example 4 produced by an

20 ordinary process.

[Reference Example 5]

63.52 parts of ammonium paramolybdate was dissolved in 300 parts of pure water at 60°C. To the solution being stirred were added, in the following

25 order, a solution of 3.46 parts of 85 mass %

phosphoric acid dissolved in 10 parts of pure water and a solution of 3.55 parts of 60 mass % arsenic acid dissolved in 10 parts of pure water. Thereto were added, in the following order, a solution of  
5 2.17 parts of copper nitrate dissolved in 10 parts of pure water and 1.75 parts of ammonium metavanadate. Thereto was added a solution of 3.64 parts of potassium nitrate dissolved in 20 parts of pure water. The resulting material was evaporated to dryness with  
10 heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed, and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air  
15 stream to obtain a catalyst. This catalyst had a composition of  $P_1Mo_{12}V_{0.5}As_{0.5}Cu_{0.3}K_{1.2}$ .

A reaction was conducted using this catalyst under the same conditions as in Reference Example 1 except that the reaction temperature was 300°C. As a  
20 result, the conversion of methacrolein was 82.4%, the selectivity of methacrylic acid was 86.9% and the per-pass yield of methacrylic acid was 71.6%.

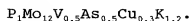
[Example 5]

In 400 parts of pure water was dispersed 94  
25 parts of a used catalyst which had been used in a

reaction for 2,000 hours under the same reaction conditions as in Reference Example 1 and which contained 34.54 parts of molybdenum, 0.93 part of phosphorus, 1.41 parts of potassium, 0.76 part of vanadium, 0.57 part of copper and 1.12 parts of arsenic and had a composition of  $P_1Mo_{12}V_{0.5}As_{0.5}Cu_{0.3}K_{1.2}$ . Thereto was added 89.0 parts of a 45 mass % sodium hydroxide solution, followed by stirring for 1 hour. The insolubles were removed by filtration. To the filtrate was added 29.6 parts of 36 mass % hydrochloric acid for pH adjustment to 9.0. Thereto was added 28.90 parts of ammonium chloride (ammonium root amount = 1.50 moles per mole of molybdenum), followed by addition of 48.4 parts of 36 mass % hydrochloric acid for pH adjustment to 5.0. The resulting mixture was kept at 60°C for 3 hours with stirring. The resulting precipitate was collected by filtration and washed with a 2 mass % ammonium nitrate solution to obtain a "recovered compound 5". The recovered compound 5 contained 25.97 parts of molybdenum, 0.56 part of phosphorus, 0.57 part of potassium, 0.38 part of vanadium, 1.12 parts of arsenic and 0.58 mole, per mole of molybdenum, of ammonium root. The recoveries of individual elements were 75.2% (molybdenum), 60.2% (phosphorus), 40.4%

(potassium), 50.0% (vanadium) and 100% (arsenic).

15.73 parts of ammonium paramolybdate was dissolved in 300 parts of pure water at 60°C. To the solution being stirred were added a solution of 1.37 parts of 85 mass % phosphoric acid dissolved in 10 parts of pure water, 4.63 parts of 25 mass % ammonia solution and the recovered compound 5. Then, there were added, in the following order, a solution of 2.17 parts of copper nitrate dissolved in 10 parts of pure water and 0.88 part of ammonium metavanadate. Thereto were added a solution of 2.16 parts of potassium nitrate dissolved in 20 parts of pure water and a solution of 1.17 parts of ammonium nitrate dissolved in 10 parts of pure water. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed and sifted using a sieve to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air stream, to obtain a catalyst. The catalyst had the same composition as in Reference Example 5, i.e.



A reaction was conducted using this catalyst under the same conditions as in Reference Example 5.

As a result, the conversion of methacrolein was 81.8%, the selectivity of methacrylic acid was 87.3% and the per-pass yield of methacrylic acid was 71.4%. Thus, the catalyst had performances equal to those of the catalyst of Reference Example 4 produced by an ordinary process.

[Reference Example 6]

In 200 parts of pure water were dissolved, at 70°C, 63.52 parts of ammonium paramolybdate, 1.75 parts of ammonium metavanadate and 7.60 parts of cesium nitrate. To the solution being stirred was added a solution of 3.55 parts of 60 mass % arsenic acid dissolved in 10 parts of pure water. Thereto was added a solution of 3.46 parts of 85 mass % phosphoric acid dissolved in 10 parts of pure water, and the resulting mixture was heated to 95°C. Thereto were added, in the following order, a solution of 2.17 parts of copper nitrate dissolved in 10 parts of pure water and a solution of 2.60 parts of cerium nitrate and 1.30 parts of lanthanum nitrate dissolved in 20 parts of pure water. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried material was subjected to pressure molding, crushed, and sifted using a sieve

to separate a moiety of 0.85 to 1.70 mm. It was heat-treated at 380°C for 5 hours in an air stream to obtain a catalyst. This catalyst had a composition of  $P_{1.2}Mo_{1.2}V_{0.5}As_{0.5}Cu_{0.3}Ce_{0.2}La_{0.1}CS_{1.3}$ .

5        A reaction was conducted using this catalyst under the same conditions as in Reference Example 1. As a result, the conversion of methacrolein was 89.8%, the selectivity of methacrylic acid was 87.6% and the per-pass yield of methacrylic acid was 78.7%.

10      [Example 6]

94 parts of the same used catalyst as in Example 5 was dispersed in 400 parts of pure water. Thereto was added 89.0 parts of a 45 mass % sodium hydroxide solution, followed by stirring for 1 hour.

15      The insolubles were removed by filtration. The filtrate was passed through a Na type chelate resin, Lewatitt TP 207 (a product of Bayer Co.) at SV = 1 to remove potassium. To the solution after passing was added 27.1 parts of 36 mass % hydrochloric acid for  
20      pH adjustment to 8.5. Then, 28.90 parts of ammonium chloride (ammonium root amount = 1.50 moles per mole of molybdenum) was added. Thereafter, 51.5 parts of 36 mass % hydrochloric acid was added for pH  
adjustment to 5.0. The resulting mixture was kept at  
25      30°C for 3 hours with stirring. The resulting

precipitate was collected by filtration and washed with a 2 mass % ammonium nitrate solution to obtain a "recovered compound 6". The recovered compound 6 contained 24.52 parts of molybdenum, 0.51 part of phosphorus, 0.33 part of vanadium, 1.12 parts of arsenic and 0.64 mole, per mole of molybdenum, of ammonium root. The recoveries of individual elements were 71.0% (molybdenum), 54.8% (phosphorus), 43.4% (vanadium) and 100% (arsenic).

In 300 parts of pure water were dissolved, at 70°C, 18.39 parts of ammonium paramolybdate, 1.00 part of ammonium metavanadate and 7.60 parts of cesium nitrate. To the solution being stirred was added the recovered compound 6. Then, a solution of 1.56 parts of 85 mass % phosphoric acid dissolved in 10 parts of pure water. Thereto was added 4.22 parts of 25 mass % ammonia solution. The resulting mixture was heated to 95°C. Thereto were added, in the following order, a solution of 2.17 parts of copper nitrate dissolved in 10 parts of pure water and a solution of 2.60 parts of cerium nitrate and 1.30 parts of lanthanum nitrate dissolved in 20 parts of pure water. The resulting mixture was evaporated to dryness with heating and stirring. The solid obtained was dried at 130°C for 16 hours. The dried



material was subjected to pressure molding, crushed  
and sifted using a sieve to separate a moiety of 0.85  
to 1.70 mm. It was heat-treated at 380°C for 5 hours  
in an air stream, to obtain a catalyst. The catalyst  
5 had the same composition as in Reference Example 6,  
i.e.  $P_{1.0}Mo_{12.0}V_{0.5}As_{0.5}Cu_{0.3}Ce_{0.2}La_{0.1}Cs_{1.3}$ .

A reaction was conducted using this catalyst  
under the same conditions as in Reference Example 6.  
As a result, the conversion of methacrolein was 89.6%,  
10 the selectivity of methacrylic acid was 88.2% and the  
per-pass yield of methacrylic acid was 79.0%. Thus,  
the catalyst had performances equal to those of the  
catalyst of Reference Example 6 produced by an  
ordinary process.

# Claims

1. A process for producing a catalyst, which comprises dispersing, in water, a used catalyst containing at least molybdenum, an A element (at  
5 least one element selected from the group consisting of phosphorus and arsenic) and an X element (at least one element selected from the group consisting of potassium, rubidium and cesium), adding thereto an alkali metal compound and/or ammonia solution, then  
10 adjusting the resulting mixture to pH 6.5 or less to generate a precipitate containing at least said molybdenum and said A element, and using the precipitate as a material for catalyst-constituting elements.
- 15 2. A process for producing a catalyst according to Claim 1, wherein the amount of the ammonium root in the mixture before adjustment to pH 6.5 or less is 0.5 mole or more relative to mole of the A element.
3. A process for producing a catalyst according to  
20 Claim 1, wherein the whole or part of the X element is removed from the mixture before adjustment to pH 6.5 or less.
4. A process for producing a catalyst according to Claim 1, wherein the precipitate is heat-treated at  
25 200 to 700°C and then used as a material for

catalyst-constituting elements.

5. A process for producing a catalyst according to Claim 1, wherein the used catalyst was, before the use, a catalyst for production of methacrylic acid by gas phase catalytic oxidation of methacrolein, having a composition represented by the following formula (1):



- (wherein Mo, V, Cu and O are molybdenum, vanadium, copper and oxygen, respectively; A is at least one element selected from the group consisting of phosphorus and arsenic; D is at least one element selected from the group consisting of antimony, bismuth, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; X is at least one element selected from the group consisting of potassium, rubidium and cesium; Y is at least one element selected from the group consisting of iron, zinc, chromium, magnesium, tantalum, manganese, cobalt, barium, gallium, cerium and lanthanum; Z is sodium and/or thallium; a, b, c, d, e, f, g, h and i are each the atomic ratio of each element; when b is 12, a=0.5 to 3, c=0.01 to 3, d=0 to 2, e=0 to 3, f=0.01 to 3, g=0 to 3, h=0 to 3, and i is the atomic ratio of oxygen necessary for satisfying the valency

of each component other than oxygen).

6. A process for producing a catalyst according to Claim 5, wherein the amount of the ammonium root in the mixture before adjustment to pH 6.5 or less is
- 5 0.5 mole or more relative to mole of the A element.
7. A process for producing a catalyst according to Claim 5, wherein the whole or part of the X element is removed from the mixture before adjustment to pH
- 6.5 or less.
- 10 8. A process for producing a catalyst according to Claim 1, wherein the produced catalyst is a catalyst for production of methacrylic acid by gas phase catalytic oxidation of methacrolein, having a composition represented by the formula (1).
- 15 9. A process for producing a catalyst according to Claim 5, wherein the produced catalyst is a catalyst for production of methacrylic acid by gas phase catalytic oxidation of methacrolein, having a composition represented by the formula (1).
- 20 10. A process for producing a catalyst according to any of Claims 1 to 9, wherein the recovery of molybdenum is 50 mass % or more and the recovery of the A element is 50 mass % or more.
11. A process for producing a catalyst according to
- 25 Claim 9, wherein the produced catalyst gives a



# Declaration and Power of Attorney For Patent Application

## 特許出願宣言書及び委任状

### Japanese Language Declaration

#### 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

Process for Production of Catalyst

上記発明の明細書は、

☐ 本書に添付されています。

the specification of which

☒ is attached hereto.

☐ \_\_\_\_月 \_\_\_\_日に提出され、米国出願番号または特許協定条

☒ was filed on May 18, 2000

約国際出願番号を \_\_\_\_ とし、

as United States Application Number or

PCT International Application Number

PCT/JP00/03184 and was amended on

☐ (該当する場合) \_\_\_\_ に訂正されました。

(if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

## Japanese Language Declaration

(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

## Prior Foreign Application(s)

外国での先行出願

11-138770	Japan
(Number)	(Country)
(番号)	(国名)
11-230058	Japan
(Number)	(Country)
(番号)	(国名)

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

## Priority Claimed

優先権主張

19/May/1999	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
(Day/Month/Year Filed)	はい	いいえ
(出願年月日)		
16/August/1999	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
(Day/Month/Year Filed)	はい	いいえ
(出願年月日)		

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.)	(Filing Date)
(出願番号)	(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

(Application No.)	(Filing Date)
(出願番号)	(出願日)

(Application No.)	(Filing Date)
(出願番号)	(出願日)

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.)	(Filing Date)
(出願番号)	(出願日)

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## Japanese Language Declaration

(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。  
(弁理士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)



022850

書類送付先

Send Correspondence to:



022850

直接電話連絡先：(名前及び電話番号)

Direct Telephone Calls to: (name and telephone number)

(703) 413-3000

単独発明者または第一の共同発明者の氏名		Full name of sole or first joint inventor Toru KURODA	
発明者の署名	日付	Inventor's signature <i>Toru Kuroda</i>	Date October 1, 2001
住所	Residence Hiroshima, Japan		
国籍	Citizenship Japanese		
郵便の宛先	Post Office Address c/o Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd., 20-1, Miyuki-cho, Otake-shi, Hiroshima 739-0693 Japan		
第二の共同発明者の氏名		Full name of second joint inventor, if any Seiichi KAWATO	
第二の共同発明者の署名	日付	Second joint inventor's signature <i>Seiichi Kawato</i>	Date October 1, 2001
住所	Residence Hiroshima, Japan		
国籍	Citizenship Japanese		
郵便の宛先	Post Office Address c/o Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd., 20-1, Miyuki-cho, Otake-shi, Hiroshima 739-0693 Japan		

(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)



## Japanese Language Declaration

(日本語宣言書)

第三の共同発明者の氏名	300	Full name of third joint inventor, if any Masanori NITTA
第三の共同発明者の署名	日付	Third joint inventor's signature Masanori Nitta Date October 1, 2001
住所		Residence Hiroshima, Japan TX
国籍		Citizenship Japanese
郵便の宛先		Post Office Address c/o Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd., 20-1, Miyuki- cho, Otake-shi, Hiroshima 739-0693 Japan

第四の共同発明者の氏名		Full name of fourth joint inventor, if any Hideyasu TAKEZAWA
第四の共同発明者の署名	日付	Fourth joint inventor's signature Hideyasu Takezawa Date October 1, 2001
住所		Residence Hiroshima, Japan TX
国籍		Citizenship Japanese
郵便の宛先		Post Office Address c/o Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd., 20-1, Miyuki- cho, Otake-shi, Hiroshima 739-0693 Japan

第五の共同発明者の氏名		Full name of fifth joint inventor, if any
第五の共同発明者の署名	日付	Fifth joint inventor's signature Date
住所		Residence
国籍		Citizenship
郵便の宛先		Post Office Address

第六の共同発明者の氏名		Full name of sixth joint inventor, if any
第六の共同発明者の署名	日付	Sixth joint inventor's signature Date
住所		Residence
国籍		Citizenship
郵便の宛先		Post Office Address

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)